

## UNIT TWO

### IDEAL GAS

#### Equation of state of a gas

In unit 1 we could see that to measure temperature precisely gas thermometer was chosen as the standard reference. This is because gas as the working substance of thermometer is far superior than mercury or platinum as the working substance. When we use mercury or platinum as the working substance of a thermometer, depending upon the quality, purity and impurity different thermometers show different temperatures. When gas is used as the working substance, in the limiting case

$\lim_{P_{TP} \rightarrow 0} \frac{P}{P_{TP}}$ , it approaches a value independent of the nature of the gas. To measure temperature we used the equation

$$T = 273.16 \lim_{P_{TP} \rightarrow 0} \frac{P}{P_{TP}} \quad \dots \dots (1)$$

It shows that whatever be the gas that we used in gas thermometers measurement is independent of the nature of the gas and gives the same value. By studying the above said behaviour of the gas experimentally in a different ways, we can arrive at the equation state of ideal gas which is the aim of this section.

Consider  $n$  moles of real gas system. Keeping its temperature constant measure the pressure  $P$  and volume  $V$  over a wide range of values. It has been found the

relation between  $PV \left( V = \frac{V}{n} \right)$  and  $P$  may be expressed as a power series of the form

$$PV = A(1 + BP + CP^2 + DP^3 + \dots) \quad \dots \dots (2)$$

This series expansion is called virial expansion and the constants  $A, B, C, D, \dots$  etc. are called first, second, third, fourth .... etc. virial coefficients respectively. The virial coefficients depend on the temperature and on the nature of the gas. It is seen experimentally that when pressure changes from 0 to 40 atm, the relation between  $PV$  and  $P$  is linear, hence virial expansion becomes

$$PV = A(1 + BP)$$

When pressure goes to higher ranges of values large number of virial coefficients will come into play.

The virial expansion gives us a very important property exhibited by the gas. To see this draw a graph between pressure on the horizontal axis and  $P_V$  along the vertical axis at a constant temperature for various gases. A typical graph of  $P_V$  versus  $P$  at boiling point of water (constant) for various gases  $O_2$ , air,  $N_2$  and  $H_2$  are drawn in figure below.

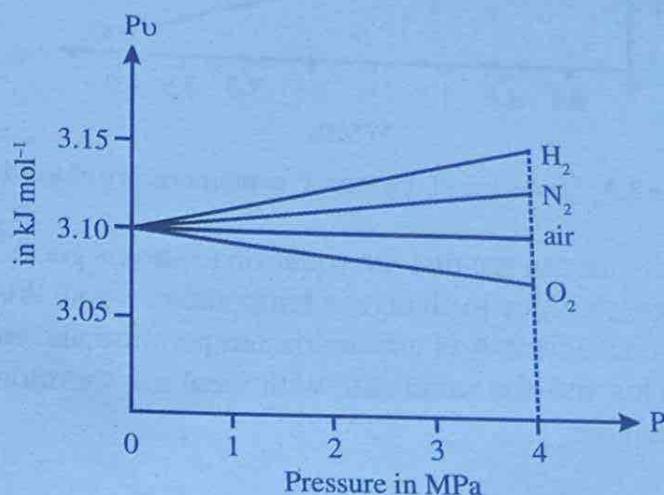


Figure 2.1 : Variation of  $P_V$  with  $P$  at boiling point of water

From the graph it is seen that for all gases as the pressure approaches zero, the product  $P_V$  approaches the same value.

Now the virial expansion becomes

$$\lim_{P \rightarrow 0} (P_V) = A \quad \dots \dots (3)$$

Where all other terms goes to zero since  $P$  goes to zero. The value of  $A$  is  $3.10 \text{ kJ mol}^{-1}$ . It shows that  $A$  is same for all gases in other words  $A$  is independent of the nature of the gases. Now repeat the same experiment for the same four gases but at different temperatures say one graph at triple point of water another at temperature at solid  $\text{CO}_2$ . Two graphs are given between.

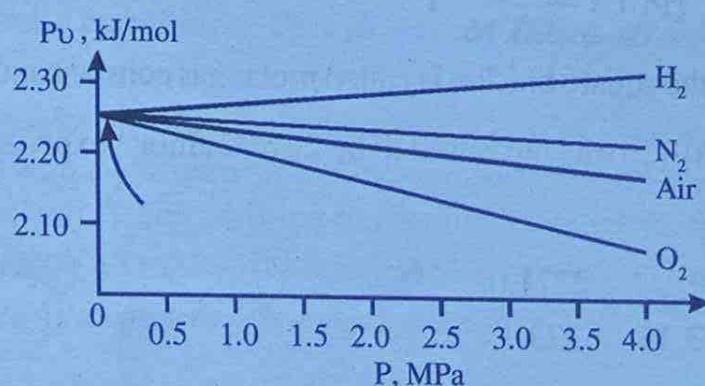


Figure 2.2 : Variation of  $P_V$  with  $P$  at triple point of water

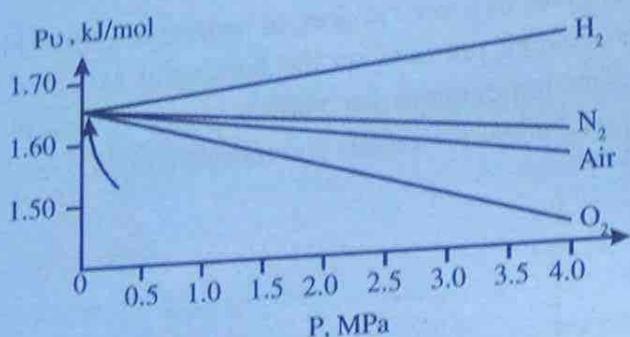


Figure 2.3 : Variation of  $P_U$  with  $P$  at temperature of solid  $\text{CO}_2$

In all three graphs we can see that the equation (3) holds good. In each graph the value of  $A$  is different. It is due to change in temperature. From this we can conclude that the first virial coefficient  $A$  is a function of temperature and independent of the nature of the gas. This was the same case with ideal gas thermometer. From ideal gas temperature, we have

$$T = 273.16 \underset{P_{TP} \rightarrow 0}{\text{Lt}} \left( \frac{P}{P_{TP}} \right) \text{ at constant volume } V.$$

Rewriting this equation as

$$T = 273.16 \underset{P_{TP} \rightarrow 0}{\text{Lt}} \left( \frac{P_U}{P_{TP} U} \right)$$

$$\text{or } T = 273.16 \frac{\text{Lt}_{P_{TP} \rightarrow 0}(P_U)}{\text{Lt}_{P_{TP} \rightarrow 0}(P_{TP} U)}$$

$$\therefore \text{Lt}_{P_{TP} \rightarrow 0}(P_U) = \frac{\text{Lt}(P_{TP} U)}{273.16} T \quad \dots \dots (4)$$

The term inside the square bracket is called molar gas constant and is denoted by  $R$ .

The value of  $(P_U)_{0^\circ\text{C}}$  was measured to be  $227.02 \text{ Jmol}^{-1}$  experimentally for oxygen

$$\text{Thus we get } \frac{(P_U)_{0^\circ\text{C}}}{273.15} = \frac{2271.02}{273.15}$$

$$= 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$$

This is the value molar gas constant. Now equation 4 becomes

$$\text{Lt } (Pv) = RT \quad \dots\dots (5)$$

That is we evaluated the virial coefficient A.

$$A = RT$$

$$\text{or} \quad \text{Lt } P \frac{V}{n} = RT$$

$$\text{Lt } PV = nRT$$

i.e., in the limit of low pressures, we have

$$PV = nRT \quad \dots\dots (6)$$

This is the equation state of an ideal gas.

Putting the value of A in the virial expansion, we get

$$Pv = RT(1 + BP + CP^2 + \dots)$$

$$\text{or} \quad \frac{Pv}{RT} = 1 + BP + CP^2 + \dots \quad \dots\dots (7)$$

This plays an important role in theoretical and experimental realm of thermodynamics.

**Note :** It must be remembered that at low pressures real gases behave like ideal gases.

### Internal energy of a real gas

In this section our aim is to find the dependence of internal energy on temperature and pressure. For this we have to perform a free expansion experiment.

### Free expansion

**When a fixed mass of gas is allowed to expand without doing any external work under adiabatic conditions. This process is called adiabatic free expansion.**

For example consider a thermally insulated vessel with rigid walls divided into two compartments with a partition wall. One compartment is filled with gas other compartment is vacuum. If the partition is removed, the gas undergoes adiabatic free expansion in which no work is done and no heat is transferred.

According to first law of thermodynamics we have

$$U_f - U_i = Q + W$$

In the adiabatic free expansion  $Q = 0$  and  $W = 0$  implies  $U_f - U_i = 0$  i.e., in free expansion there is no change in internal energy. Then what happens to temperature and pressure. First experimental attempt in this was made by Joule in 1843. He tried to measure  $\left(\frac{\partial T}{\partial V}\right)_V$  which is called the Joule coefficient. Joule coefficient tells us how does the temperature of system change with volume during adiabatic free expansion.

### Joules experiment

Experimental arrangement consists of two flasks A and B connected by a tube and fitted with a stop cock S as shown in figure below. A was filled with a gas at higher pressure and B was perfectly evacuated. The whole system was immersed in a water bath. The temperature of water bath was measured with a sensitive thermometer. The stop-cock was opened and the gas rushed from A to B. The temperature of water bath was again measured.

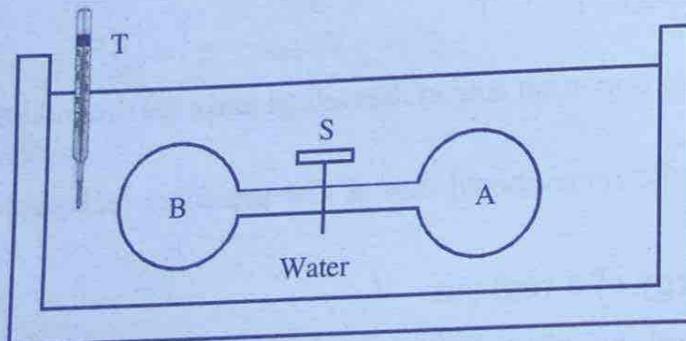


Figure 2.4 : Joules experimental setup

The idea was to measure the drop in temperature of the gas by measuring the temperature of water bath. Since the pressure and volume of the gas change normally we expect a drop in temperature. But in this experiment no temperature drop was measured. Joule could point out the draw back of his experiment and the difficulty in measuring  $\left(\frac{\partial T}{\partial V}\right)_V$ .

Thus a new method was suggested, instead of measuring a temperature change during free expansion for which the internal energy is constant, consider measuring a change of internal energy at constant temperature.

We know that internal energy  $U$  is a function of any two of the three thermodynamic coordinates  $P$ ,  $V$  and  $T$ .

If  $U$  is a function of  $(T, V)$ , we have

$$U = U(T, V)$$

Taking differentials, we get

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

When no temperature change ( $dT = 0$ ) occurs in free expansion ( $dU = 0$ )

We get  $\left( \frac{\partial U}{\partial V} \right)_T = 0$  ..... (8)

It shows that  $U$  is independent of volume

If we consider  $U$  is a function of  $T$  and  $P$

$$U = U(T, P)$$

Then  $dU = \left( \frac{\partial U}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial P} \right)_T dP$

When there is no temperature change ( $dT = 0$ ) occurs in free expansion in which  $dU = 0$ , we get

$$\left( \frac{\partial U}{\partial P} \right)_T = 0 . \quad \dots \dots (9)$$

It shows that  $U$  is independent of pressure. Clubbing the statements of the two equations 8 and 9  $U$  is independent of  $V$  and  $P$ . Therefore  $U$  is a function of  $T$  only.

Now we have to conduct an experiment to prove that  $U$  is a function of temperature only. In this experiment we want to verify that

$$\left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\partial U}{\partial P} \right)_T = 0 \text{ at constant temperature.}$$

### Experimental setup

This experiment was firstly conducted by Rossini and Frandsen in 1932 after 90 years of Joules experiment.

The experimental arrangement consists of a bottle B containing  $n$  moles of gas at pressure  $P$ . The gas communicates with the atmosphere through a long coil wrapped around the bottle as shown in figure. The whole apparatus is immersed in water bath whose temperature is maintained constant at exactly the same value as that of the surroundings.

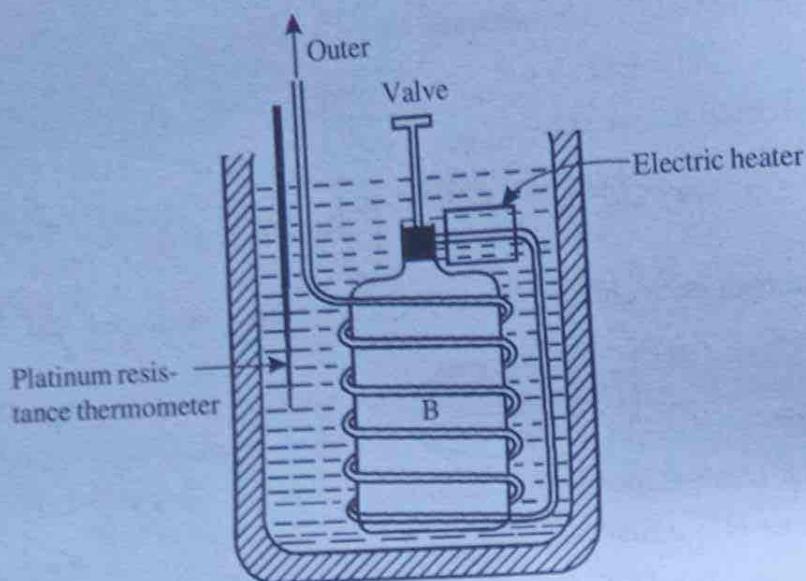


Figure 2.5 : Apparatus for measuring  $(\partial u / \partial P)_T$  of a gas. (F.D. Rossini and M Frandsen)

To begin the experiment the valve attached to the bottle is opened slightly. The gas will escape to air slowly through the coil. At the same time the temperature of the gas, the bottle, the coils and the water is maintained constant by an electric heating coil immersed in the water. The electrical energy supplied to the water is equal to the heat  $Q$  absorbed by the gas during the expansion. The work done by the gas is (whole gas is leaked out)

$$W = -PdV$$

$$\text{i.e., } W = -P_0(nv_0 - V)$$

where  $P_0$  is the atmospheric pressure,  $v_0$  is molar volume at atmospheric pressure and temperature and  $V$  is the volume of the bottle.

If  $u(P, T)$  is the molar energy at pressure  $P$  and temperature  $T$  and if  $u(P_0, T)$  is the molar internal energy at atmospheric pressure and the same temperature. Using first law of thermodynamics

$$U_f - U_i = Q + W$$

$$\text{i.e., } nu(P, T) - nu(P_0, T) = Q + W$$

$$\text{or } u(P, T) - u(P_0, T) = \frac{Q + W}{n}$$

The change in internal energy  $\Delta u$  for various values of  $P$  are measured. A graph

is plotted between  $\Delta u$  on the vertical axis and P on the horizontal axis, a straight line graph is obtained as shown in figure below. Since  $u(P_0, T)$  is a constant, the slope of the resulting curve is equal to  $\left(\frac{\partial u}{\partial P}\right)_T$ , at any value of P. Within the pressure change of 1 to 40 standard atmospheres the slope  $\left(\frac{\partial u}{\partial P}\right)_T$  is the same for all pressures. It shows that  $\left(\frac{\partial u}{\partial P}\right)_T$  is independent of the pressure, depending only on the temperature. Thus, we have  $\left(\frac{\partial u}{\partial P}\right)_T = f(T)$ . This implies that u is a function of both pressure and temperature. The experiments were repeated for various gases such as air, oxygen, and mixtures of oxygen and carbon dioxide they obtained the same result.

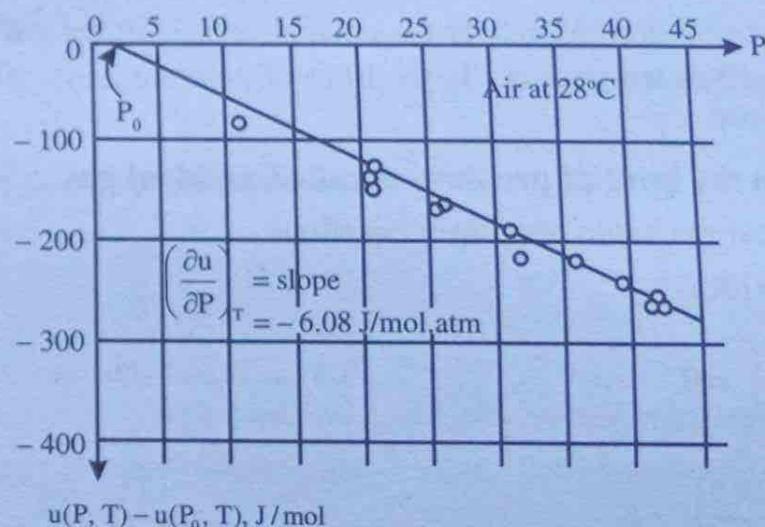


Figure 2.6 : Dependence of change of molar internal energy of a real gas on pressure, where  $P_0$  is atmospheric pressure

They also found no pressure or temperature range in which  $\left(\frac{\partial U}{\partial P}\right)_T = 0$

$$\text{i.e., } \left(\frac{\partial U}{\partial P}\right)_T \neq 0$$

$$\text{writing } \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial V}\right)_T$$

For free expansion at constant temperature  $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$  and we proved that

$$\left(\frac{\partial U}{\partial P}\right)_T \neq 0.$$

The above equation shows that  $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$ . For a real gas  $\left(\frac{\partial U}{\partial P}\right)_T \neq 0$  and  $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$ . For a perfect gas we will prove that  $\left(\frac{\partial U}{\partial P}\right)_T = 0$  and  $\left(\frac{\partial U}{\partial V}\right)_T = 0$

At the same time we know that a real gas behaves like an ideal gas in the limit of pressure. In our experiment since limiting pressure is not reached the gas behaved as such.

### Ideal gas

We found that a real gas whose pressure  $P \rightarrow 0$ , the equation of state assumes a simple form  $PV = nRT$ . Moreover the internal energy of real gas is a function of pressure as well as temperature. In the limit of pressure,  $U$  is only a function of temperature only.

**A real gas in the limit of pressure is called an ideal gas**

Thus an ideal gas has to obey three equations

(i)  $PV = nRT$

(ii)  $\left(\frac{\partial U}{\partial P}\right)_T = 0$

(iii) and  $\left(\frac{\partial U}{\partial V}\right)_T = 0$

The third equation follows from equation (ii).

i.e.,  $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$

For an ideal gas

$$PV = nRT$$

Differentiating the above with respect to  $V$ , keeping  $T$  constant, we get

$$P + V \left( \frac{\partial P}{\partial V} \right)_T = 0$$

or  $\left( \frac{\partial P}{\partial V} \right)_T = -\frac{P}{V}$

since  $\left( \frac{\partial U}{\partial P} \right)_T = 0$  and  $\left( \frac{\partial P}{\partial V} \right)_T \neq 0$ , we can very well write  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ .

From (ii) and iii, we can write

(iv)  $U = f(T)$  only

**Note:** Limiting pressure means very low pressure.

Ideally  $P \rightarrow 0$ . Pressure is very low even at about 2 atmospheres real gas behaves like ideal gas without much error.

### Mayers relation

Consider an hydrostatic system (ideal) which undergoes an infinitesimal quasi-static process, according to first law.

$$dQ = dU + PdV \quad \dots \dots (10)$$

Using  $\left( \frac{\partial P}{\partial T} \right)_V = C_V$

For ideal gas  $U$  is a function of only  $T$ .

i.e.,  $\frac{dU}{dT} = C_V$

or  $dU = C_V dT$

Now equation 10 becomes

$$dQ = C_V dT + PdV \quad \dots \dots (11)$$

From the ideal gas equation, we have

$$PV = nRT$$

For infinitesimal quasi-static process

$$PdV + VdP = nRdT$$

$$\text{or } PdV = nRdT - VdP$$

put this in equation 11, we get

$$dQ = C_v dT + nRdT - VdP \quad \dots\dots (12)$$

Dividing by  $dT$ ,

$$\frac{dQ}{dT} = C_v + nR - V \frac{dP}{dT}$$

At constant pressure

$$\left( \frac{dQ}{dT} \right)_p = C_v + nR$$

By definition

$$\left( \frac{dQ}{dT} \right)_p = C_p$$

$$\therefore C_p = C_v + nR$$

$$\text{or } C_p - C_v = nR \quad \dots\dots (13)$$

This is called Mayer's relation. The equation 13 tells us that  $C_p$  is always greater than  $C_v$ . This is because when heat is supplied to a gas and allowed to expand at constant pressure heat is used for two purposes.

- (i) It raises the temperature of the gas (i.e., increase in internal energy) and
- (ii) it does work in expanding the gas against the external pressure we have  
 $dQ = dU + PdV$ .

On the other hand, when gas is heated at constant volume, no work is done (i.e.,  $dW = 0$ ) and hence whole of heat supplied is used to raise its temperature.

$$\text{i.e., } dQ = dU = C_v dT$$

$$\text{Thus } C_p > C_v$$

One more useful equation can be obtained from equation 12

$$\text{i.e., } dQ = C_v dT + nRdT - VdP$$

$$\text{or } dQ = (C_v + nR)dT - VdP$$

From Mayer's relation

$$C_p - C_v = nR$$

or  $C_p = C_v + nR$

$$\therefore dQ = C_p dT - V dP \quad \dots\dots (14)$$

### Experimental determination of heat capacities

Heat capacities of real gases are usually measured by the electric method.

#### Measurement of $C_v$

The gas whose  $C_v$  is to be measured is taken in a thin walled steel flask with a heating coil wound around it. Measure the initial temperature of the gas as  $T_i$  by a sensitive thermometer. Pass a suitable current  $I$  for a time  $t$ .

The heat supplied by the heat coil.  $Q = VIt$ , where  $V$  is the potential difference given to the heating coil. This heat is transferred to the gas and temperature of the gas rises. Let it be  $T_f$ . The heat absorbed by the gas is

$$Q = C_v(T_f - T_i)$$

Using law of conservation of energy we have  $VIt = C_v(T_f - T_i)$

$$\therefore C_v = \frac{VIt}{(T_f - T_i)}$$

knowing  $V$ ,  $I$ ,  $t$  and  $T_f - T_i$ ,  $C_v$  can be calculated.

To measure  $C_p$  the gas is allowed to flow at constant pressure through a calorimeter where it receives heat ( $VI$ ) per second. From the initial (inlet) and the final (outlet) temperatures the value of  $C_p$  can be calculated as before. Use  $C_p$  instead of  $C_v$ .

Since the measurements are done at low pressure  $C_p$  and  $C_v$  measured are those of ideal gas. The following may be worth noting.

1. For all ideal gases

- a)  $C_v$  is a function of  $T$
- b)  $C_p$  is a function of  $T$
- c)  $C_p > C_v$
- d)  $C_p - C_v = R$ , independent of  $T$

- e)  $\frac{C_p}{C_v} = \gamma$  is a function of T and greater than 1
2. For monatomic gases such as He, Ne and Ar
- $C_v$  is constant over a wide range of temperature and its value  $C_v = \frac{3}{2}R$  (nearly)
  - $C_p$  is constant over a wide range of temperature and its value  $C_p = \frac{5}{2}R$  (nearly)
  - $\frac{C_p}{C_v} = \gamma$  is constant over a wide range and is nearly equal to  $\frac{5}{3}$ .
3. For diatomic gases such as air,  $H_2$ ,  $O_2$ ,  $N_2$ , NO, CO etc.,
- $C_v = \frac{5}{2}R$ , constant for ordinary temperatures and increases as the temperature is raised
  - $C_p = \frac{7}{2}R$ , constant at ordinary temperatures and increases as the temperature is raised.
  - $\frac{C_p}{C_v} = \frac{7}{5}$ , constant at ordinary temperatures and decreases as the temperature is raised.
4. For polyatomic gases such as  $CO_2$ ,  $NH_3$ ,  $CH_4$ ,  $Cl_2$ ,  $Br_2$  etc.  $C_p$ ,  $C_v$  and  $\frac{C_p}{C_v}$  vary with temperature, the variation is different for each gas.

**Note:** The behaviour of  $H_2$  is exceptional.  $H_2$  is diatomic hence  $C_p = \frac{7}{2}R$ . But very low temperature  $C_p = \frac{5}{2}R$  i.e., behaves like monatomic gas. For all diatomic gases except hydrogen,  $\frac{C_p}{R}$  can be written as

$$\frac{C_p}{R} = \frac{7}{2} + f(T)$$

form of  $f(T)$  is  $\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{(e^{b/T} - 1)^2}$

### Quasi-static adiabatic process

When an ideal gas undergoes a quasi-static adiabatic process pressure P, volume V and temperature T may change. But to write down equation of state we require only any two combinations (P, V), (T, V) and (P, T).

### Equation of state

Recall equation 11 and 14

$$dQ = C_v dT + P dV$$

$$dQ = C_p dT - V dP$$

In an adiabatic process  $dQ = 0$

$$\therefore C_v dT = -P dV \quad \dots\dots (15)$$

$$\text{and } C_p dT = -V dP \quad \dots\dots (16)$$

$$\frac{\text{Eq 16}}{\text{Eq 15}} \text{ gives } \frac{C_p}{C_v} = -\frac{V dP}{P dV}$$

$$\text{or } \gamma = -\frac{V dP}{P dV}$$

$$\text{or } \frac{\gamma dV}{V} = -\frac{dP}{P}$$

The equation cannot be integrated as  $\gamma$  depends on temperature. But most of the adiabatic processes temperature change is moderate. Assume that  $\gamma$  is constant and integrate, we get

$$\gamma \ln V = -\ln P + C$$

$$\text{or } \ln P + \ln V^\gamma = C$$

$$\ln P V^\gamma = C$$

$$\text{or } P V^\gamma = \text{constant} \quad \dots\dots (17)$$

This is the equation of state of a quasi-static adiabatic process in terms of P and V

### Equation of state in terms of P and T

We have  $PV = nRT$

$$\text{or } V = \frac{nRT}{P}$$

Putting this in equation 17, yields

$$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant}$$

$$\text{or } \frac{T^{\gamma}}{P^{\gamma-1}} = \text{constant}$$

$$\text{or } \frac{P^{\gamma-1}}{T^{\gamma}} = \text{constant} \quad \dots\dots (18)$$

### Equation of state in terms of T and V

From  $PV = nRT$

$$P = \frac{nRT}{V}$$

Put this in equation 17, yields

$$\frac{nRT}{V} V^{\gamma} = \text{constant}$$

$$\text{or } TV^{\gamma-1} = \text{constant} \quad \dots\dots (19)$$

**Note:** It may be noted that an adiabatic free expansion process is not quasistatic, hence equations 17, 18 and 19 are not valid for this process.

### Slopes of adiabatics and isothermals

In an isothermal process

$$PV = \text{a constant}$$

Taking the differential on both sides we get

$$PdV + VdQ = 0$$

$$\text{or } \frac{dP}{dV} = -\frac{P}{V}$$

$\frac{dP}{dV}$  is the slope

$$\text{i.e., } \left( \frac{dP}{dV} \right)_{\text{iso}} = -\frac{P}{V}.$$

In an adiabatic process

$$PV^\gamma = \text{a constant}$$

Taking the differential on both sides, we get

$$P\gamma V^{\gamma-1}dV + V^\gamma dP = 0$$

$$\text{or } \frac{dP}{dV} = -\frac{\gamma P}{V}$$

$$\text{i.e., } \left( \frac{dP}{dV} \right)_{\text{adi}} = -\frac{\gamma P}{V}$$

Comparing the slopes of isothermal and adiabatic, we get

$$\left( \frac{dP}{dV} \right)_{\text{adi}} = \gamma \left( \frac{dP}{dV} \right)_{\text{iso}}$$

i.e., slope of adiabatic is  $\gamma$  times the slope of the isothermal. Hence adiabatic curve is steeper than the isothermal curve. See figure above

### Isothermal and adiabatic elasticity of a gas

#### Isothermal elasticity ( $E_{\text{iso}}$ )

Suppose we have a certain mass of gas enclosed in a cylinder of a perfectly conducting material, fitted with a piston of the same material, so that its temperature throughout remains constant. Let its volume be  $V$  and its pressure  $P$ .

Now let the pressure  $P$  be increased slightly to  $P + dP$ , so that the volume of the gas is reduced to  $V - dV$

Stress applied by the gas =  $dP$

$$\text{Strain produced} = \frac{\text{change in volume}}{\text{original volume}} = \frac{dV}{V}$$

$$\therefore \text{Elasticity} = \frac{\text{stress}}{\text{strain}} = \frac{dP}{dV}$$

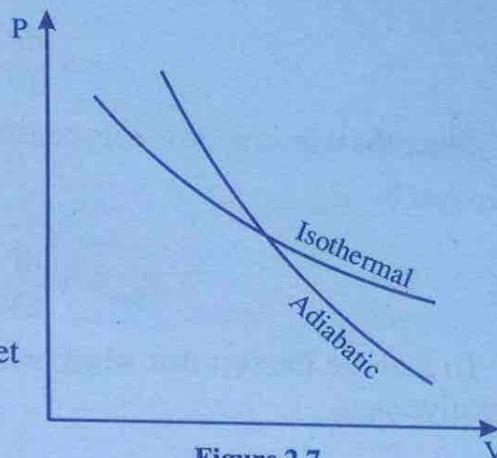


Figure 2.7

$$= V \frac{dP}{dV}$$

Since the temperature is kept constant here, it is called isothermal elasticity and is denoted by  $E_{iso}$

i.e.  $E_{iso} = V \frac{dP}{dV}$

To indicate the fact that when pressure increases the volume decreases we put a negative sign.

$$\therefore E_{iso} = -V \frac{dP}{dV} \quad \dots\dots (20)$$

For an isothermal process, we have

$$PV = K$$

Taking differentials on both sides, we get

$$PdV + VdP = 0$$

or  $P = -V \frac{dP}{dV}$

Thus  $E_{iso} = P \quad \dots\dots (21)$

This shows that isothermal elasticity of a gas is equal to its pressure.

### Adiabatic elasticity ( $E_{adi}$ )

We have  $E = -V \frac{dP}{dV}$

Suppose the system undergoes an adiabatic process, then the elasticity is called adiabatic elasticity.

i.e.  $E_{adi} = -V \frac{dP}{dV}$

During an adiabatic process, we have

$$PV^\gamma = K$$

Taking differentials on both sides, we get

$$P\gamma V^{\gamma-1} dV + d(PV^\gamma) = 0$$

Dividing throughout by  $V^{\gamma-1}$ , we get

$$P\gamma dV + dPV = 0$$

or

$$-V \frac{dP}{dV} = \gamma P$$

$$\therefore E_{\text{adia}} = \gamma P \quad \dots\dots (22)$$

This shows that adiabatic elasticity of a gas is equal to  $\gamma$  times its pressure.

Comparing eq (21) and eq (22) we get

$$E_{\text{adi}} = \gamma E_{\text{iso}} \quad \dots\dots (23)$$

The reason for  $E_{\text{adia}} > \gamma E_{\text{iso}}$  is that for similar change in pressure  $dP$ , there is a larger change in volume for the adiabatic process.

### The microscopic point of view

Here we discuss the limitations of classical thermodynamics based on macroscopic point of view and need for microscopic point of view.

The first law of thermodynamics which is the relation connecting between work, heat and internal energy. This can be applied to class of systems such as solids, liquids, vapours, mixture of substances etc. The solution of the first law does not give properties of a particular system. For example we measure  $C_V$  of a system given by

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

This is true for all hydrostatic systems. If we know the internal energy we can calculate  $C_V$ , where  $C_V$  is a function of  $T$  and  $V$ . Thus the heat transferred during an isochoric process is

$$Q_V = \int_{T_i}^{T_f} C_V dT, \text{ provided } C_V \text{ is known. But in classical thermodynamics nothing}$$

provides detailed information of  $U$  and  $C_V$ . This one of the major limitations.

Another limitation is that classical thermodynamics is unable to provide the equation of state of any desired system. To have an equation of state involving  $P$ ,  $V$ ,  $T$

and the derivatives  $\left( \frac{\partial P}{\partial V} \right)_T$ ,  $\left( \frac{\partial V}{\partial T} \right)_P$  and  $\left( \frac{\partial T}{\partial P} \right)_V$  are required. These values must

come from the experimental results. For each system we have to conduct experiments to evaluate those derivatives. Experimental datas for all systems are not available.

So to obtain informations regarding thermal properties of system without having to experimental measurements we go for analysing the system at microscopic level. We require calculations based on the properties and behaviour of particles of the system. There are two such theories developed. One is the kinetic theory and the other one is statistical mechanics. Using laws of mechanics and statistics kinetic theory deals with the average motion of particles and their collisions in order to calculate the equation of state for the ideal gas. But statistical mechanics deal with average value of energy of particles or ensemble of particles. Once the energy is obtained we can develop equation of state and thermodynamic variables and functions.

### Kinetic theory of ideal gas

Here our aim is to formulate a microscopic theory of ideal gases limited to monoatomic gases. To develop the theory several assumptions are made. The assumptions are called postulates.

### Postulates of kinetic theory of gases

1. Any sample of gas consists of an enormous number of atoms  $N$ . For any gas all atoms are identical and inert. If  $m$  is the mass of each atom, the total mass is  $mN$ .

If  $M$  be the molar mass, then the number of moles  $n = \frac{Nm}{M}$ . The number of

atoms per mole is  $\frac{M}{m} = \frac{N}{n}$  is called Avagadro's number denoted  $N_A$ . Its value is calculated by Avagadro and is given by  $N_A = 6.0221 \times 10^{23}$  atoms/mole.

2. The atoms are assumed to be small hard spheres and they are in ceaseless random motion. The average distance between neighbouring atoms is large compared to the size of the atom.

For example the size of the atom is of the order of 2 or  $3 \times 10^{-10}$  m. The average distance between atoms is about 50 times diameter under standard pressure and temperature.

3. It is due to the large distance between atoms it is also assumed that there are no interatomic force of attraction or repulsion between atoms. Forces come into play only when atoms collide with one another and also with walls. Between collisions they move with uniform rectilinear motion.

4. The walls of the container is assumed to be smooth and the collision is assumed to perfectly elastic. If  $v$  is the speed of an atom approaching a wall, the perpendicular component  $v_{\perp}$  is retraced back with same velocity, therefore total change in velocity is  $-2v_{\perp}$
5. When there is no external field of force, the atoms are distributed uniformly throughout the system. So that the number density  $\frac{N}{V}$  is a constant. In any small element of volume  $dV$ , there are  $dN$  atoms, where

$$\frac{dN}{dV} = \frac{N}{V} \text{ or } dN = \frac{N}{V} dV$$

The infinitesimal  $dV$  must satisfy two conditions of infinitesimal in thermodynamics.  $dV$  must be small compared to  $V$  and large enough to make  $dN$  a large number.

6. Since the motion of atom is random there is no preferred direction for the velocity. All directions are equally probable.
7. Atoms move with different speed varying from 0 to any value.

With these assumptions we can arrive at an interpretation for temperature in terms of kinetic energy

Consider cubical box ABCDEFGH of side  $l$  contains certain amount of ideal gas. The volume of the gas is  $l^3$ . Let  $m$  and  $N$  represent the mass of each atom and number of atoms respectively present in the box.

Consider an atom  $P$  moving in a random direction with a velocity  $c_1$ . This velocity can be resolved into three components  $u_1$ ,  $v_1$  and  $w_1$  along the X, Y and Z axis respectively (see figure).

$$c_1^2 = u_1^2 + v_1^2 + w_1^2$$

The velocity with which the atom  $P$  strikes the face BCFG is  $u_1$  and the

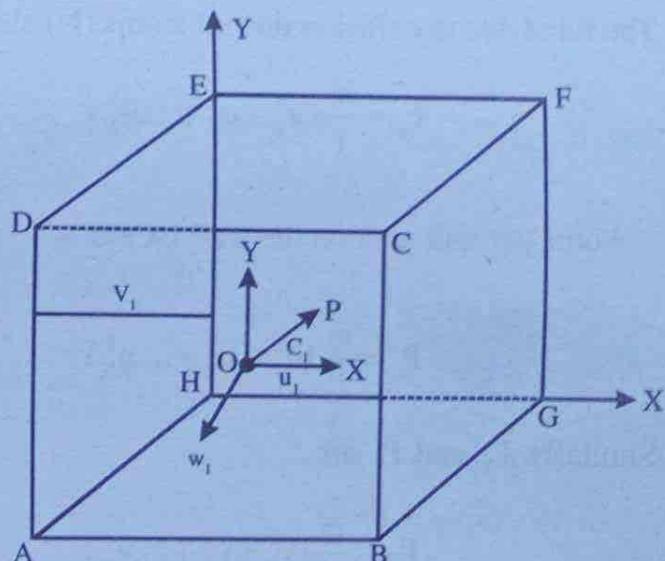


Figure 2.8

corresponding momentum is  $mu_1$ . It is due to elastic collision the atom is reflected with the same momentum.

The change in momentum due to the impact of collision

$$= mu_1 - (-mu_1) = 2mu_1$$

The atom reflected from BCFG travels a distance  $l$  towards ADEH strikes on this wall again reflected back to hit on BCFG. The total distance travelled by the atom when it collides with the wall BCFG is  $2l$ .

$\therefore$  The time interval between two successive collisions on the wall BCFG is

$$= \frac{\text{distance}}{\text{speed}} = \frac{2l}{u_1}$$

$$\therefore \text{Number of collisions per second} = \frac{1}{2l} = \frac{u_1}{2l}$$

$$\therefore \text{Change in momentum produced in 1 second} = 2mu_1 \cdot \frac{u_1}{2l} = \frac{mu_1^2}{l}$$

The force due to collision due all atoms ( $N$ ) along the X-direction is

$$F_x = \frac{m}{l} (u_1^2 + u_2^2 + \dots u_N^2)$$

$$\therefore \text{Force per unit area on the wall BCFG is } P_x = \frac{F_x}{l^2}$$

$$\text{or } P_x = \frac{m}{l^3} (u_1^2 + u_2^2 + \dots u_N^2)$$

Similarly  $P_y$  and  $P_z$  are

$$P_y = \frac{m}{l^3} (v_1^2 + v_2^2 + \dots v_N^2)$$

$$\text{and } P_z = \frac{m}{l^3} (w_1^2 + w_2^2 + \dots w_N^2)$$

As the pressure is same in all directions the average pressure is

$$P = \frac{P_x + P_y + P_z}{3}$$

i.e.,  $P = \frac{m}{3l^2} [(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) + \dots (u_N^2 + v_N^2 + w_N^2)]$

$$P = \frac{m}{3l^2} (c_1^2 + c_2^2 + c_n^2) \quad \dots \dots (24)$$

Let  $c$  be the root mean square velocity of the atoms

$$c^2 = \frac{c_1^2 + c_2^2 + \dots c_N^2}{N}$$

or

$$Nc^2 = c_1^2 + c_2^2 + \dots c_N^2$$

Put this in equation 24 we get

$$P = \frac{m}{3l^2} Nc^2$$

or

$$P = \frac{mNc^2}{3V} \quad (\because l^3 = \text{volume})$$

or

$$PV = \frac{1}{3} mNc^2 \quad \dots \dots (25)$$

From the experimental results of thermodynamics, we deducted the equation of state of ideal gas given by

$$PV = nRT \quad \dots \dots (26)$$

Comparing equations 25 and 26, we get

$$nRT = \frac{1}{3} mNc^2 \quad \dots \dots (27)$$

or

$$T = \frac{mN}{nR} \frac{1}{3} c^2$$

This can be re-written as

$$T = \frac{2N}{3R} \left( \frac{1}{2} mc^2 \right) \quad \dots \dots (28)$$

$\frac{1}{2}mc^2$  is the average kinetic energy of the atoms. Thus we have

$$\text{kinetic energy} \propto T$$

It provides an interpretation of temperature on the basis of kinetic theory. In kinetic theory of gases we assumed that there are no inter atomic forces. Hence particles posses no potential energy. So the entire energy is kinetic. Moreover we also assumed that atoms are in rectilinear motion. Thus this energy is purely translational kinetic energy. The monatomic gas possesses no rotational or vibrational energies. Therefore the internal energy (U) of a monatomic gas is the sum of the kinetic energies of all atoms.

$$\text{i.e., } U = \sum_i \frac{1}{2}m_i c_i^2$$

$$\text{or } U = \frac{Nm}{2} \sum_i c_i^2$$

$$U = N \frac{1}{2} m \sum_i c_i^2 = N \frac{1}{2} mc^2$$

Substituting for  $\frac{1}{2}mc^2$  from equation 27, we get

$$U = \frac{N}{2} \frac{3nRT}{N}$$

$$\text{or } U = \frac{3n}{2} RT \quad \dots\dots (29)$$

It shows that internal of ideal gas is proportional to temperature only which is in agreement with experimental results.

From equation 29 we can calculate  $C_V$  and  $C_P$ .

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} nR \quad \dots\dots (30)$$

Using  $C_P - C_V = nR$

$$C_P - \frac{3}{2} nR = nR$$

or

$$C_p = \frac{5}{2} nR \quad \dots\dots (31)$$

Equations 30 and 31 show that  $C_v$  and  $C_p$  are independent of temperature.

Using  $n = \frac{N}{N_A}$ , the equation can be written as

$$U = \frac{3}{2} \frac{N}{N_A} RT$$

The term  $\frac{R}{N_A} = 1.3807 \times 10^{-27} \text{ JK}^{-1}$  is called Boltzmann's constant denoted by  $k$ .

$$U = \frac{3N}{2} kT \quad \dots\dots (32)$$

$\therefore$  Average kinetic per atom is

$$\frac{U}{N} = \frac{3}{2} kT$$

or  $\frac{1}{2} mc^2 = \frac{3}{2} kT$

$$\therefore \text{The rms velocity } c = \sqrt{\frac{3kT}{m}} \quad \dots\dots (33)$$

**Note :** In the case of diatomic and poly atomic gases they possess rotational and vibrational kinetic energies in addition to translational kinetic energy. As there is no interaction, potential energy is zero.

$$\text{In general } U = \frac{nRT}{\gamma - 1}, \gamma = \frac{C_p}{C_v}$$

The ideal gas equation  $PV = nRT$  is not obeyed by real gases, particularly at high pressures and low temperatures. In the derivation of the ideal gas equation on the basis of kinetic theory of gases two assumptions that have been made which do not hold good in case of real gases. They are (i) atoms are point masses and (ii) there are no interatomic forces. But in actual practice, at high pressure size of the atom becomes significant and cannot be neglected in comparison with the volume of the

gas. Also at high pressure the atoms comes closer and interatomic forces are appreciable. Hence ideal gas equation needs modification. So in 1881, Vander Waal proposed an equation of state that accounted for the finite volume of the atoms and interaction between the atoms. The Vander Waals equation of state is

$$\left( P + \frac{n^2 a}{V^2} \right) (V - b) = nRT$$

Where the constant  $a$  accounts for interatomic force between the atoms and  $b$  accounts for volume correction. It is due to the finite size of atoms, the actual volume available for the movement of atoms is less than the volume of  $V$  of the vessel.  $P$  appearing in Vander Waals equation is the observed pressure. It is due to correction observed pressure decreases.

Vander Waals equation of state is not valid for all real gas. After that several equations of state had been proposed such as claussius equation of state, Berthelot equation of state, Dieterici equation of state, Saba and Bose equation of state and so on. None was perfectly correct.

### Example 1

Expand the Vander Waals equation of state,  $\left( P + \frac{a}{v^2} \right) (v - b) = RT$  in virial series form.

### Solution

$$\left( P + \frac{a}{v^2} \right) (v - b) = RT$$

$$P \left( 1 + \frac{a}{Pv^2} \right) v \left( 1 - \frac{b}{v} \right) = RT$$

or

$$Pv = \frac{RT}{\left( 1 + \frac{a}{Pv^2} \right) \left( 1 - \frac{b}{v} \right)}$$

i.e.,

$$Pv = RT \left( 1 - \frac{b}{v} \right)^{-1} \left( 1 + \frac{a}{Pv^2} \right)^{-1}$$

Since  $\frac{b}{v}$  and  $\frac{a}{Pv^2}$  are very small we can apply Bionomial approximation

$$PV = RT \left( 1 + \frac{b}{v} \right) \left( 1 - \frac{a}{Pv^2} \right)$$

$$PV = RT \left( 1 + \frac{b}{v} - \frac{a}{Pv^2} - \frac{ab}{Pv^3} \right)$$

The term  $\frac{ab}{Pv^3}$  is negligibly small

$$PV = RT \left( 1 + \frac{b}{v} - \frac{a}{Pv} \right)$$

The second and third terms on the R.H.S are correction terms. Then we can use  
 $PV = RT$

In the second term put  $v = \frac{RT}{P}$  and in the third term put  $PV = RT$

$$\therefore PV = RT \left( 1 + \frac{bP}{RT} - \frac{a}{RTv} \right)$$

or  $PV = RT \left( 1 + \frac{b}{RT} P - \frac{a}{R^2 T^2} P \right)$

$$PV = \left( 1 + \left( \frac{b}{RT} - \frac{a}{R^2 T^2} \right) P \right)$$

This is the required form,

### Example 2

Write down the Dieterici equation of state,  $Pe^{\frac{RT}{RT-b}}(v-b)=RT$  in the virial form

### Solution

$$Pe^{\frac{RT}{RT-b}}(v-b)=RT$$

$$PV - Pb = RT e^{-\frac{RT}{RT-b}}$$

$$PV = Pb + RT e^{-\frac{RT}{RT-b}}$$

Expanding the exponential term

$$Pv = Pb + RT \left( 1 - \frac{a}{RTv} \right)$$

Retained only linear term.

$$Pv = RT \left[ 1 - \frac{a}{RTv} + \frac{Pb}{RT} \right]$$

If we substitute  $v = \frac{RT}{P}$  for the second correction term, we get

$$Pv = RT \left[ 1 - \frac{aP}{R^2 T^2} + \frac{Pb}{RT} \right]$$

or  $Pv = RT \left[ 1 + \left( \frac{b}{RT} - \frac{a}{R^2 T^2} \right) P \right]$

**Note :** Look at the answers of example (1) and (2), they are same.

### Example 3

If the pressure of an ideal gas varies according to the equation  $P = P_0 - aV^2$ , where  $P_0$  and  $a$  are constants find the maximum attainable temperature.

### Solution

$$P = P_0 - aV^2$$

Using  $PV = nRT$ ,  $V = \frac{nRT}{P}$

$$\therefore P = P_0 - \frac{an^2 R^2 T^2}{P^2}$$

$$P^3 = P_0 P^2 - an^2 R^2 T^2 \quad \dots\dots (1)$$

Differentiating with respect to  $P$  we get

$$3P^2 = 2P_0 P - an^2 R^2 2T \frac{dT}{dP}$$

For maximum temperature  $\frac{dT}{dP} = 0$

$$3P = 2P_0$$

$$P = \frac{2}{3}P_0$$

Put this in equation (1), we get

$$\left(\frac{2}{3}P_0\right)^3 = P_0 \left(\frac{2}{3}P_0\right)^2 - an^2R^2 T_{\max}^2$$

$$an^2R^2 T_{\max}^2 = \frac{4}{9}P_0^3 - \frac{8}{27}P_0^3$$

$$an^2R^2 T_{\max}^2 = \frac{4}{27}P_0^3$$

$$T_{\max} = \frac{2}{3\sqrt{3}} \frac{P_0^{3/2}}{\sqrt{anR}}$$

$$T_{\max} = \frac{2}{3} \left( \frac{P_0}{nR} \right) \sqrt{\frac{P_0}{3a}}$$

It may be checked that  $\frac{d^2T}{dP^2}$  is negative.

#### Example 4

Find the minimum attainable pressure of ideal gas in the process  $T = T_0 + aV^2$ , where  $T_0$  and  $a$  are constant

#### Solution

$$T = T_0 + aV^2 \text{ given}$$

$$\text{Using } PV = nRT, T = \frac{PV}{nR}$$

$$\frac{PV}{nR} = T_0 + aV^2$$

or  $P = \frac{nT_0 R}{V} + anR V$  ..... (1)

so  $\frac{dP}{dV} = -\frac{nT_0 R}{V^2} + anR$

For minimum pressure  $\frac{dP}{dV} = 0$ , yields

$$\frac{nT_0 R}{V^2} = anR$$

$$V = \sqrt{\frac{T_0}{a}} \text{ put this in equation (1)}$$

$$P_{\min} = \frac{nT_0 R}{\sqrt{\frac{T_0}{a}}} + anR \sqrt{\frac{T_0}{a}}$$

$$P_{\min} = nR\sqrt{aT_0} + nR\sqrt{T_0 a}$$

$$P_{\min} = 2nR\sqrt{aT_0}$$

It may be checked that  $\frac{d^2 P}{dV^2}$  is positive.

### Example 5

Prove that the work done by an ideal gas with constant heat capacity  $C_V$  during a quasi-static adiabatic expansion is  $W = -C_V(T_f - T_i)$

### Solution

We have  $dQ = dU + dW$

or  $dQ = C_V dT + dW$

For an adiabatic process  $dQ = 0$

$$\therefore dW = -C_V dT$$

integrating  $W = - \int_{T_i}^{T_f} C_V dT = -C_V (T_f - T_i)$

### Example 6

Show that the heat transferred during an infinitesimal quasi-static process of a ideal gas can be written as

$$dQ = \frac{C_V V dP}{nR} + \frac{C_P}{nR} \cdot P dV$$

### Solution

We have  $dQ = dU + PdV$

or  $dQ = C_V dT + PdV$  ..... (1)

From ideal gas equation of state

$$PV = nRT$$

Take differentials on both sides, yields

$$PdV + VdP = nRdT$$

or  $dT = \frac{PdV + VdP}{nR}$

Put this in equation (1), we get

$$dQ = C_V \frac{(PdV + VdP)}{nR} + PdV$$

$$dQ = \frac{C_V V dP}{nR} + \frac{C_V P dV}{nR} + PdV$$

$$dQ = \frac{C_V V dP}{nR} + PdV \left( \frac{C_V}{nR} + 1 \right)$$

or  $dQ = \frac{C_V V dP}{nR} + \frac{PdV}{nR} (C_V + nR)$

Using  $C_P - C_V = nR$ ,  $C_P = C_V + nR$

$$\therefore dQ = \frac{C_V V dP}{nR} + \frac{P dV}{nR} C_P$$

**Example 7**

Calculate the internal energy of the air in your room of volume  $40\text{m}^3$ . Assume that air behaves like ideal gas

**Solution**

We have  $U = \frac{nRT}{\gamma - 1}$

For ideal gas  $PV = nRT$

$$\therefore U = \frac{PV}{\gamma - 1} = \frac{1 \times 10^5 \times 40}{1.4 - 1} = 10^7 \text{ J}$$

$$= 10\text{MJ}$$

**Example 8**

If  $h$  is the height above sea level show that the decrease of atmospheric pressure due to rise of  $dh$  is given by

$$\frac{dP}{P} = -\frac{Mg}{RT} dh$$

where  $M$  is the molar mass of air,  $g$  is the acceleration of gravity and  $T$  is the temperature at height  $z$ .

**Solution**

Consider a layer of thickness of air  $dh$  at  $h$  height above the surface of the earth. The pressures acting on the two sides of the layer are shown in the figure. Equating the upward and downward forces, we get

$$Adh\rho g + (P + dP)A = PA$$

or

$$dP = -\rho g dh$$

Using  $PV = RT$

$$\frac{PM}{\rho} = RT \text{ gives } \rho = \frac{PM}{RT}$$

$$\therefore dP = -\frac{PMgdh}{RT}$$

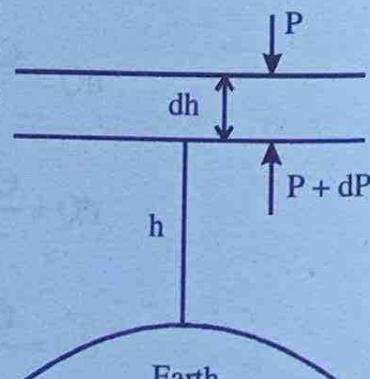


Figure 2.9

or

$$\frac{dP}{\rho} = -\frac{Mgdh}{RT}$$

Integrating this we get the variation of pressure with height

$$\int_{P_0}^P \frac{dP}{\rho} = -\frac{Mg}{RT} \int_0^h dh$$

$$\ln \frac{P}{P_0} = -\frac{Mgh}{RT}$$

$$P = P_0 e^{-\frac{Mgh}{RT}}$$

In this derivation temperature is assumed to be constant.

### Example 9

A horizontal cylinder closed at one end and is rotated with a constant angular velocity  $\omega$  about a vertical axis passing through the open end of the cylinder. The outside pressure is  $P_0$  and temperature T and the molar mass of air is M. Find the air pressure as a function of the distance r from the rotation axis. Assume that molar mass is independent of mass.

### Solution

The centripetal force on the thin layer of thickness  $dr$  is

$$F = (P + dP)A - PA$$

$$mr\omega^2 = dPA$$

$$A\rho dr r\omega^2 = dPA$$

$$\therefore dP = \rho\omega^2 r dr \quad \dots\dots (1)$$

$$PV = RT$$

$$P = \frac{\rho}{M} RT \quad \dots\dots (2)$$

$\frac{\text{Eq 1}}{\text{Eq 2}}$  gives

$$\frac{dP}{P} = \frac{M\omega^2}{RT} r dr \text{ Integrating}$$

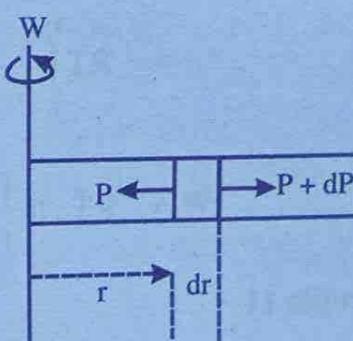


Figure 2.10

$$\int_{P_0}^P \frac{dP}{P} = \frac{M\omega^2}{RT} \int_0^r r dr$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{M\omega^2 r^2}{2RT}$$

$$P = P_0 e^{\frac{M\omega^2 r^2}{2RT}}$$

**Example 10**

Find the work performed by one mole of a Vander Waals gas during its isothermal expansion from the volume  $V_1$  to  $V_2$  at temperature  $T$ .

**Solution**

We have  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$  for 1 mole.

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\begin{aligned} \text{Work done} &= - \int_{V_1}^{V_2} P dV \\ &= - \int_{V_1}^{V_2} \left( \frac{RT}{V - b} - \frac{a}{V^2} \right) dV \\ &= - RT \int_{V_1}^{V_2} \frac{1}{V - b} dV + \int_{V_1}^{V_2} \frac{a}{V^2} dV \\ W &= - RT \ln \frac{(V_2 - b)}{(V_1 - b)} - a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

**Example 11**

Air is compressed adiabatically to half its volume. Calculate the change in temperature. Initial temperature is  $27^\circ C$ .

**Solution**

$$\text{Initial volume} = V, \text{ Final volume} = \frac{V}{2}$$

$$\text{Initial temperature} = 27^\circ\text{C} = 27 + 273 + 300 \text{ K}$$

Using

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$300(V)^{\frac{7}{5}-1} = T_2 \left(\frac{V}{2}\right)^{\frac{7}{5}-1}$$

$$300V^{\frac{2}{5}} = T_2 2^{-\frac{2}{5}} \cdot V^{\frac{2}{5}}$$

$$\begin{aligned} T_2 &= \frac{300}{2^{-\frac{2}{5}}} = 300 \times 1.319 \\ &= 395.85 \text{ K} \end{aligned}$$

$$\therefore \text{Change in temperature} = 395.85 - 300 = 95.85 \text{ K} \\ = 95.85^\circ\text{C}.$$

**Note :** Since air is diatomic,  $\gamma = \frac{7}{5}$

**Example 12**

A quantity of air at  $27^\circ\text{C}$  and one atmospheric pressure is suddenly compressed half its original volume. Find the final pressure.

**Solution**

$$P_1 = 1 \text{ atm}, \quad V_1 = V, \quad V_2 = \frac{V}{2}$$

Using

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$P_1 V^\gamma = P_2 \left(\frac{V}{2}\right)^\gamma$$

$$P_2 = P_1 2^\gamma$$

$$P_2 = 1 \times 2^{1.4} = 1.263 \text{ atm}$$

**Example 13**

A tyre pumped to a pressure of 3 atm suddenly bursts. Calculate the fall in temperature due to adiabatic expansion. Initial temperature  $27^\circ\text{C}$  and  $\gamma = 1.4$

**Solution**

$$P_1 = 3 \text{ atm}, P_2 = 1 \text{ atm} \text{ and } T_1 = 27 + 273 = 300 \text{ K}$$

$$\gamma = 1.4 = \frac{7}{5}$$

Using

$$T_1^{\gamma} P_1^{1-\gamma} = T_2^{\gamma} P_2^{1-\gamma}$$

or

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\frac{T_2^{\gamma}}{300^{\gamma}} = \left(\frac{1}{3}\right)^{\gamma-1}$$

$$T_2 = \left(\frac{1}{3}\right)^{\frac{\gamma-1}{\gamma}} \cdot 300$$

$$T_2 = \left(\frac{1}{3}\right)^{\frac{2}{7}} \times 300$$

$$\therefore \frac{\gamma-1}{\gamma} = \frac{\frac{7}{5}-1}{\frac{7}{5}} = \frac{2}{7}$$

$$= 219.2 \text{ K}$$

$$\begin{aligned} \therefore \text{Fall in temperature} &= T_1 - T_2 \\ &= 300 - 219.2 \\ &= 80.8 \text{ K.} \end{aligned}$$

**Example 14**

The initial temperature of a gas is  $27^\circ\text{C}$ . Calculate the temperature when the gas is compressed suddenly to 8 times its original pressure ( $\gamma = 1.5$ ).

**Solution**

$$T_1 = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$P_2 = \frac{P_1}{8} \text{ and } \gamma = 1.5$$

Using

$$\frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma}$$

or

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^\gamma$$

$$\left(\frac{8P_1}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{300}\right)^\gamma$$

$$8^{\gamma-1} = \left(\frac{T_2}{300}\right)^\gamma$$

$$8^{0.5} = \left(\frac{T_2}{300}\right)^{\frac{3}{2}}$$

or

$$8^{\frac{1}{3}} = \frac{T_2}{300}$$

$$(2^3)^{\frac{1}{3}} = \frac{T_2}{300}$$

or

$$T_2 = 600 \text{ K}$$

### Example 15

A gas occupying 1 litre at 80 cm of Hg pressure is expanded adiabatically to 1190 cc. If the pressure falls to 60 cm of Hg in the process, deduce the value of  $\gamma$ .

### Solution

$$V_1 = 1 \text{ litre} = 10^3 \text{ cc}, P_1 = 80$$

$$V_2 = 1190 \text{ cc}, P_2 = 60$$

Using

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$80 \times (10^3)^\gamma = 60(1190)^\gamma$$

or  $\frac{80}{60} = \left(\frac{1190}{1000}\right)^\gamma$

$$\frac{4}{3} = (1.190)^\gamma$$

or  $\log \frac{4}{3} = \gamma \log 1.190$

$$\gamma = \frac{\log \frac{4}{3}}{\log 1.19} = \frac{0.125}{0.0755} = 1.66$$

$$\gamma = 1.66$$

### IMPORTANT FORMULAE

1. Temperature of ideal gas

$$T = 273.16 \underset{P_{TP} \rightarrow 0}{\text{Lt}} \left( \frac{P}{P_{TP}} \right)$$

2. Virial expansion

$$PV = A(1 + BP + CP^2 + DP^3 + \dots)$$

A, B, C, D ..... etc. are virial coefficients

$$\underset{P \rightarrow 0}{\text{Lt}} (PV) = A = RT$$

3. Molar gas constant

$$\underset{273.16}{\text{Lt}} \frac{(PV)}{T_P} = R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

4. Ideal gas equation

$$PV = nRT$$

5. For isothermal adiabatic free expansion

$$\left( \frac{\partial U}{\partial P} \right)_T = 0 \text{ and } \left( \frac{\partial U}{\partial V} \right)_T = 0, U = f(T)$$

6. For a real gas

$$\left(\frac{\partial U}{\partial P}\right)_T \neq 0 \text{ and } \left(\frac{\partial U}{\partial V}\right)_T \neq 0$$

7. Mayer's relation:  $C_p - C_v = nR$

8. Two important relations

$$dQ = C_v dT + P dV$$

$$dQ = C_p dT - V dP$$

9. Equation of state of quasi-static adiabatic process

$$(i) \quad PV^\gamma = \text{constant}$$

$$(ii) \quad \frac{P^{\gamma-1}}{T^\gamma} = \text{constant}$$

$$(iii) \quad TV^{\gamma-1} = \text{constant}$$

10. Slopes of adiabatics and isotherms

$$(i) \quad \left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{P}{V}$$

$$(ii) \quad \left(\frac{dP}{dV}\right)_{\text{adi}} = -\frac{\gamma P}{V} \text{ or } \left(\frac{dP}{dV}\right)_{\text{adi}} = \gamma \left(\frac{dP}{dV}\right)_{\text{iso}}$$

11. Isothermal and adiabatic elasticities

$$(i) \quad E_{\text{iso}} = -V \left(\frac{dP}{dV}\right)_T = P$$

$$(ii) \quad E_{\text{adi}} = -V \left(\frac{dP}{dV}\right)_{\text{adi}} = \gamma P \text{ or } E_{\text{adi}} = \gamma E_{\text{iso}}$$

12. Relation between temperature and kinetic energy

$$T = \frac{2N}{3R} \left( \frac{1}{2} mc^2 \right)$$

13. Expression for internal energy and heat capacity of monatomic ideal gas.

$$U = \frac{3}{2} nRT, \quad C_v = \frac{3}{2} nR$$

$$\text{or } U = \frac{3N}{2}kT \quad C_V = \frac{3}{2}Nk$$

14. Vander Waal's equation of state

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

## UNIVERSITY MODEL QUESTIONS

### Section A

(Answer questions in about two or three sentences)

#### **Short answer questions**

1. What is the basis of arriving at equation of state of ideal gas?
2. Write down the virial series expansion of real gas and explain the symbols.
3. Draw  $P_U$  versus  $P$  graph at constant temperature in the range 0 to  $4 \times 10^6 \text{ Pa}$ .
4. Define molar gas constant. What is its unit and value.
5. Under what conditions ideal gas equation is valid.
6. What is meant by adiabatic free expansion?
7. Show that the internal energy of a system remains the same when it undergoes free adiabatic expansion.
8. Define the Joule coefficient.
9. In an isothermal, free expansion express internal energy in terms of pressure.
10. On what all thermodynamic coordinates the internal energy of a real gas depend.
11. Define ideal gas.
12. Write down three equations that ideal gas satisfy.
13. Write down Mayer's relation and explain the symbols used.
14. Explain why  $C_p > C_v$ .
15. Why a gas has two heat capacities?
16. Write down the properties of molar heat capacities of ideal gases.
17. Write down  $C_p, C_v$  for a monatomic ideal gas.
18. Write down the temperature dependence of  $C_p, C_v$  and  $\gamma$  for a diatomic gas.
19. What is the exceptional behaviour of  $C_p$  of hydrogen atom?
20. Write down the three equations of state of quasi-static adiabatic process.
21. What are isotherms?
22. What are adiabatics?

23. Define (i) isothermal elasticity and (ii) adiabatic elasticity of a gas.
24. Mention two limitations of classical thermodynamics.
25. Write down the Vander Waals equation and explain the symbols used.
26. Write down an expression for the internal energy of a monatomic gas and obtain  $C_v$ .

### Section B

(Answer questions in about half a page to one page)

#### Paragraph / problem type

1. Briefly explain Joule's experiment.
2. Show that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  and  $\left(\frac{\partial U}{\partial P}\right)_T = 0$  for an isothermal free expansion.
3. Derive the relation  $C_p - C_v = nR$
4. Briefly explain the experimental determination of  $C_v$  by electric method.
5. Derive the equation of state of a quasi-static adiabatic process.
6. Show that adiabatic slope is steeper than isothermal slope.
7. Show that adiabatic elasticity is  $\gamma$  times isothermal elasticity.
8. What are the limitations of classical thermodynamics?
9. What were the assumptions made in the kinetic theory of gases?
10. Explain the reason for the modification of ideal gas equation.
11. Write down the Berthelot equation of state  $\left(P + \frac{a}{v^2 T}\right)(v - b) = RT$  in the virial form.
12. The pressure of an ideal gas varies according to the relation  $P = P_0 e^{-\beta v}$  where  $P_0$  and are constants. Find the maximum attainable temperature  $\left(T_{\max} = \frac{P_0}{n e \beta R}\right)$
13. Prove that the work done by an ideal gas with constant heat capacities during a quasi-static expansion is equal to  $W = \frac{P_f V_f}{\gamma - 1} \left[ 1 - \left( \frac{P_i}{P_f} \right)^{\frac{\gamma-1}{\gamma}} \right]$
14. An open glass tube of uniform cross section is bent in to the shape of an L. One arm is immersed a liquid of density  $\rho$ , the other arm of length remains in the air in a horizontal position. The tube is rotated with a constant angular speed  $\omega$  about the axis of the vertical arm. Prove that the height  $h$  to which the liquid rises in the vertical arm is equal to  $h = \frac{P_0}{\rho g} \left( 1 - e^{-\frac{\omega^2 L^2 M}{2RT}} \right)$ .

15. A volume of a gas expands isothermally to 4 times its initial volume. Calculate the work done by the gas. [1.387 RT]
16. One mole of a monoatomic perfect gas ( $\gamma = \frac{5}{3}$ ) is adiabatically compressed from an initial pressure of 1 atmosphere to a final pressure of 150 atmospheres. Assuming the initial temperature of the gas to be 27°C. Calculate work done on the gas during compression ( $1\text{ atm} = 10^5 \text{ Nm}^{-2}$ ) [2.397  $\times 10^4 \text{ J}$ ]
17. One mole of a gas at 127°C expands isothermally until its volume is doubled. Find the amount of work done. [2301J]
18. A sample of an ideal gas is expanded to twice its original volume of  $1\text{ m}^3$  in a quasi static process for which  $P = KV^2$ , where K is a constant whose value is  $5 \text{ atm/m}^6$ . Calculate the work done by the gas. [11.78  $\times 10^5 \text{ J}$ ]
19. A quantity of air ( $\gamma = 1.4$ ) at 27°C is compressed suddenly to  $\frac{1}{4}$  th of its volume. Find the final temperature. [522.3K]
20. One mole of nitrogen expands isothermally at 20°C from a volume of 10 litre to 20 litre. Find how much heat must be supplied to keep the temperature from dropping.  $R = 8.3 \text{ J/mol.K}$  [1685.7 J]
21. One mole of helium at 27°C is compressed adiabatically so that pressure becomes 32 times its initial value. Find the final temperature and work done  $R = 8.3 \text{ J/mol.K}$  and  $\gamma = \frac{5}{3}$  [1200 K, 11205 J]

### Section C

(Answer question in about two pages)

#### Long answer type questions-Essays

1. Describe Rossini and Frandsen experiment and prove that internal energy is a function of pressure, volume and temperature.
2. Based on the kinetic theory of gases arrive at the relation between temperature and kinetic energy.

#### Hints to problems

$$11. \left( P + \frac{a}{Tb^2} \right) (v - b) = RT$$

$$P \left( 1 + \frac{a}{PTv^2} \right) v \left( 1 - \frac{b}{v} \right) = RT$$

$$PV = \frac{RT}{\left(1 - \frac{b}{V}\right)\left(1 + \frac{a}{PTV^2}\right)}$$

$$PV = RT \left(1 - \frac{b}{V}\right)^{-1} \left(1 + \frac{a}{PTV^2}\right)^{-1}$$

$$PV = RT \left[\left(1 + \frac{b}{V}\right) \left(1 - \frac{a}{PTV^2}\right)\right]$$

$$PV = RT \left[1 + \frac{b}{V} - \frac{a}{PTV^2}\right]$$

Use  $PV = RT$  on the correction terms

$$PV = RT \left(1 + \frac{bP}{RT} - \frac{aP}{R^2T^3}\right)$$

$$PV = RT \left[\left(1 + \frac{b}{RT} - \frac{a}{R^2T^3}\right)P\right]$$

12.  $P = P_0 e^{-\beta V}$  use  $P = \frac{nRT}{V}$

$$\frac{nRT}{V} = P_0 e^{-\beta V}$$

$$T = \frac{P_0 V}{nR} e^{-\beta V} \quad \text{Find } \frac{dT}{dV} = 0 \quad \frac{d^2T}{dV^2} \text{ is -ve}$$

Find  $T_{\max}$ .  $T$  is maximum at  $V = \frac{1}{\beta}$ .

13. We know that the adiabatic work done is

$$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

$$W = \frac{P_f V_f}{\gamma - 1} \left[1 - \frac{P_i}{P_f} \frac{V_i}{V_f}\right] \quad \dots\dots (1)$$

In an adiabatic process the equation of state is  $PV^\gamma = \text{constant}$

or  $P_i V_i^\gamma = P_f V_f^\gamma$

$$\frac{V_i^\gamma}{V_f^\gamma} = \frac{P_f}{P_i}$$

$$\frac{V_i}{V_f} = \left( \frac{P_f}{P_i} \right)^{\frac{1}{\gamma}}$$

Put this in equation (1), we get the required result.

14.  $hpg = P_0 - P$ ,  $P$  emerges from centripetal force is calculated in example 10.

$$15. W = -RT \ln \frac{V_2}{V_1} = -RT \ln \frac{4V}{V} = -RT \ln 4 \\ = -1.386RT$$

Negative work indicates work is done by the system.

$$16. \frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma} \quad P_1 = 1, P_2 = 150, T_1 = 300 \\ \therefore T_2 = 2226 \text{ K}$$

$$\text{Work done } W = \frac{R}{\gamma-1} (T_2 - T_1)$$

$$R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$W = 2.397 \times 10^4 \text{ J}$$

Work done positive indicate work is done on the system.

17.  $T = 127 + 273 > 300 \text{ K}$

$$W = -RT \ln \frac{V_2}{V_1}, R = 8.3$$

$$W = -2301 \text{ J}$$

Negative work done indicates work is done by the system.

$$18. \text{ Work done, } W = - \int_{V_1}^{V_2} P dV = - \int_1^2 KV^2 dV \\ K = 5 \times 10^5$$

$$\therefore W = -11.78 \times 10^5 \text{ J}$$

Negative work done indicates work is done by the system.

$$19. T_1 = 27 + 273 = 300 \text{ K}, V_2 = \frac{V_1}{2}$$

Using  $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$T_2 = 522.3\text{K.}$$

20. We have

$$dQ = dU + dW = dU + PdV = C_v dT + PdV$$

$$dQ = PdV \quad (\because dT = 0)$$

$$\begin{aligned} Q &= \int PdV = RT \ln \frac{V_2}{V_1} \\ &= 1685.7\text{J} \end{aligned}$$

21.  $\frac{P_1^{\gamma-1}}{T_1^{\gamma-1}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma-1}}$

$$P_1 = P, P_2 = 32P$$

$$T_1 = 300\text{K}$$

$$\therefore T_2 = 1300\text{K}$$

$$\begin{aligned} \text{Work done } W &= \frac{R}{\gamma-1} [T_2 - T_1] \\ &= 11205\text{J} \end{aligned}$$

Positive work indicates work is done on the system.

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